

PATENT SPECIFICATION

(11) 1 373 937

- (21) Application No. 60067/71 (22) Filed 23 Dec. 1971
 (31) Convention Application No. 2 063 734 (32) Filed 24 Dec. 1970 in
 (33) Germany (DT)
 (44) Complete Specification published 13 Nov. 1974
 (51) International Classification C08F 45/00; C08H 9/10
 (52) Index at acceptance

C3P 7C12A 7C13A 7C13B 7C14A 7C16A 7C17 7C18
 7C20A 7C20B 7C20C 7C20D2 7C3 7C5 7C7
 7D1A 7D2A1 7K8 7T2D 7T2X 8C12A 8C13A
 8C13B 8C14A 8C16A 8C17 8C18 8C20A 8C20B
 8C20C 8C20D2 8C3 8C5 8C7 8D1A 8D2A 8K7
 8T2D E2
 B1V 2A2 3D2 3F
 C5W 5D 8A1 8A3 8B1 8B2



(54) WAXES FOR USE IN EMULSIONS

(71) We, FARBWERKE HOECHST AKTIENGESSELLSCHAFT, vormals Meister Lucius & Brüning, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt (Main) 80, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to waxes that are particularly suited for use in emulsions for floors.

Oxidised polyethylene or copolymers of ethylene with other monomers, emulsified with olein and volatile amines, are used for the preparation of self-polishing emulsions on the basis of polyethylene waxes. Olein and volatile amines, however, have certain well known disadvantages in this respect. Olein causes softening of wax films made from the emulsions and thus adversely affects their property of being walked upon. Amines are relatively expensive and sometimes contribute toward discoloration of the films; the volatility of the amines can also disturb the preparation of the emulsions.

Polyethylene waxes may, however, be emulsified without olein and amines, by being reacted (saponified) in the melt with potassium hydroxide and mixed with non-ionic emulsifiers (*Soap and Chemical Specialities* 1970 No. 3, p. 128). The wax melt obtained is then processed by the wax-in-water process to form an ionic/non-ionic self-polishing emulsion, formulated in known manner using polymer dispersions and ammoniacal solutions of wetting resins as well as other common additives, to obtain a marketable polishing emulsion.

Tests have shown that the above-mentioned process and the waxes obtained thereby have certain disadvantages. The wax cannot be processed directly from the melt by a method suited for industrial application, since, by

[Price 25p]

virtue of its pronounced tackiness, it can be neither stocked in the form of lumps nor formed into scales for commercial use. Thus it cannot be used as a solid wax but only as a melt, directly after preparation, for the manufacture of self-polishing emulsions. Furthermore, the melt has a high melting viscosity, of more than 1500 cp (120°C) and can therefore only be emulsified by the wax-in-water process; the emulsification is generally incomplete or does not yield a sufficiently fine dispersion. The water-in-water process requires a greater expenditure on equipment than does the water-in-wax process and many emulsion manufacturers are therefore not in a position to use it. A further disadvantage is the discoloration that sometimes occurs while reacting the polyethylene wax with the potassium hydroxide.

The present invention provides a wax suitable for use in an ionic/non-ionic self-polishing emulsion and comprising:

- (a) from 10 to 65% of an oxidised ethylene polymer or of an oxidised copolymer of ethylene and unsaturated fatty acid units, having a dropping point of from 95 to 115°C, an acid number of from 3 to 90, and a molecular weight of from 1500 to 4000;
 - (b) from 10 to 65% of an ester wax having an acid number of from 4 to 80;
 - (c) from 15 to 65% of a hydrocarbon wax; and
 - (d) from 5 to 25% of at least one polyethylene glycol ether of (i) an alkylphenol having from 3 to 16 carbon atoms in the alkyl moiety, or (ii) a fatty amine having from 8 to 24 carbon atoms, or (iii) a fatty alcohol having from 8 to 24 carbon atoms;
- components (a) and (b) having been saponified with from 0.8 to 3.2% of potassium hydroxide, and all percentages being based on

the total weight of components (a), (b) and (c).

The use of the mixture of components (a), (b) and (c), instead of polyethylene wax alone (component (a)), for the saponification, enables the afore-mentioned disadvantages to be substantially overcome.

The wax of the invention is a hard clear product, generally having a low melting viscosity of from 40 to 700, preferably from 70 to 500, cP (120°C) thus enabling it to be processed, without any additives by either the wax-in-water or water-in-wax method, preferably the latter, to form a finely dispersed stable emulsion.

Component (a) of the wax of the invention is an oxidized wax-like ethylene polymer or an oxidized wax-like copolymer of ethylene and an unsaturated fatty acid. Such polymers or copolymers may be obtained by known methods by oxidation of a synthetic or degraded wax or by copolymerization of ethylene and, for example, crotonic, acrylic or methacrylic acid. These wax-like products have a dropping point of from 95 to 115°C, an acid number of from 3 to 90, preferably from 10 to 50, and a molecular weight of from 1500 to 4000.

The ester wax, component (b), is preferably a so-called "partially synthetic" ester wax, which may be obtained, for example, by esterification of an oxidation product of deresinated or non-deresinated crude montan wax with a monohydric or polyhydric aliphatic alcohol. A natural wax, for example carnauba wax, may alternatively be used. The wax (whether natural or synthetic) has an acid number of from 4 to 80, preferably from 20 to 40.

Component (c) is generally a hard non-oxidized hydrocarbon wax made from crude oil, for example a micro-crystalline wax having a melting point of from 80 to 90°C, a density (at 20°C) of from 0.93 to 0.95 g/cm³, and a penetration number (according to Richardson) of from 4 to 10.

Component (d) is a non-ionic emulsifier and consists of at least one polyethylene glycol ether of an alkylphenol having from 3 to 16 carbon atoms in the side chain or of a fatty amine or fatty alcohol each having from 8 to 24 carbon atoms in the molecule. Such ethers may be obtained by ethoxylation of the respective phenol, amine or alcohol, the phenol component being, for example, nonylphenol or tributylphenol, the fatty amine component being, for example, stearylamine, oleylamine or coconut fatty amine, and the fatty alcohol component being, for example, stearyl alcohol, tallow fatty alcohol or *iso*-tridecyl alcohol. The ether preferably contains from 4 to 30 moles of ethylene oxide per mole of phenol, amine or alcohol. A single emulsifier or a mixture of emulsifiers may be used.

Components (a) and (b), in admixture with component (c), of the wax of the invention, are saponified with from 0.8 to 3.2%

of potassium hydroxide, based on the total weight of components (a), (b) and (c).

The wax of the invention can be easily formed into the industrially preferred scales. The wax is suitable for use in an emulsion, preferably a self-polishing emulsion. Such an emulsion may additionally contain one or more of the following components: a polymer dispersion (for example, one on the basis of styrene-acrylate), a wetting and levelling agent (for example a colophonium- or styrene-maleic resin or a fluorocarboxylic acid), a plastifier (for example dibutylphthalate, tributoxo-ethyl-phosphate, methyl-diglycol, ethyl-diglycol or ethylene glycol), a preservative, a metal salt, an anti-corrosion agent, an anti-freeze agent, and a surface-active substance.

The present invention also provides a process for the preparation of a wax, which process comprises mixing component (a), (b) and (c), as defined above in the amounts specified above, saponifying the mixture with potassium hydroxide, and, either before, after or during the saponification or in portions before, after and/or during the saponification, mixing component (d), as defined above in the amount specified above, with the mixture.

The wax may suitably be prepared as follows: the ester wax, the ethylene polymer or copolymer and the micro-crystalline wax, and optionally the emulsifier or a portion thereof, are mixed in the melt at a temperature of from 105° to 120°C with agitation; subsequently potassium hydroxide is added and the temperature is raised to about 125°C over a period of about 30 minutes; if necessary, the emulsifier or the remaining portion thereof is then added.

From 0.8 to 3.2% of potassium hydroxide is used. Generally a stock aqueous solution of given concentration is used; thus from 2 to 7%, based on the sum weight of components (a), (b) and (c) of a 43% potassium hydroxide solution may, for example, be used.

The raising of the temperature while adding the potassium hydroxide aids the removal of water formed during the reaction and of water introduced with the potassium hydroxide. Reduced pressure may optionally be used further to aid this removal.

The following Examples 1 and 2 illustrate the prior art using a polyethylene wax alone. Examples 3 and 4 illustrate the waxes of the present invention. The waxes of all four Examples were emulsified and the properties of the waxes and the emulsions prepared therefrom are listed in the Table. Examples 5 to 7 illustrate the manufacture of self-polishing emulsions from the wax emulsion prepared in Example 3. Parts and percentages are by weight.

Example 1.

76.0 parts of a copolymer made from ethylene and acrylic acid (acid number 48)

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and 18.5 parts of oxethylated nonylphenol (10 moles of ethylene oxide per mole of nonylphenol) were heated to 110°—120°C and saponified with 5.5 parts of a 43% potassium hydroxide solution. The wax melt obtained was emulsified according to the water-in-wax method. It was not possible to completely emulsify the wax; thus its intrinsic gloss and light transmittance could not be measured.

10 Example 2.

71.5 parts of an oxidized polyethylene wax (acid number 15, molecular weight from 2000 to 3000) and 21.5 parts of oxethylated nonylphenol (9 moles of ethylene oxide per mole of nonylphenol) were heated to 110°—120°C and saponified with a mixture of 1.5 parts of potassium hydroxide and 5.5 parts of ethylene glycol. The wax melt obtained was emulsified according to the water-in-wax method. It was not possible to completely emulsify the wax, and therefore its intrinsic gloss and light transmittance could not be measured.

25 Example 3.

23.0 parts of an ester wax made from crude montan wax and ethylene glycol (acid number 28), 27.0 parts of a copolymer made from ethylene and acrylic acid (acid number of 48), 32.5 parts of a hard, non-oxidized micro-crystalline wax (penetration number 7, melting point 82°C, density 0.940 at 20°C), and 10.5 parts of nonylphenol oxyethylated with 6 moles of ethylene oxide, were mixed in the melt at 110°C. The mixture was then carefully saponified, while stirring, with 3.5 parts of a 43% potassium hydroxide solution and subsequently stirred for a further 30 minutes at 125°C. Subsequently, 3.5 parts of oxethylated stearylamine (10 moles of ethylene oxide per mole of amine) were stirred in. The mixture was then transformed into marketable scales by means of a scaling roll. The wax so obtained could be emulsified according to the water-in-wax process by slowly adding 85.0 parts of

water at 95°C, while stirring, to 15.0 parts of the wax melt heated to 115°C. 45

Example 4.

28.0 parts of a clear ester wax made from crude montan wax and ethylene glycol (acid number 30), 29.0 parts of an oxidized polyethylene wax (acid number 15, dropping point 101°C), 26.0 parts of a hard, non-oxidized micro-crystalline wax (penetration number 6.5, melting point 83°C, density 0.941 at 20°C), and 10.0 parts of nonylphenol oxethylated with 6 moles of ethylene oxide, were saponified, as described in Example 3, with 3.5 parts of a 43% potassium hydroxide solution. 3.5 parts of oxethylated stearylamine (10 moles of ethylene oxide per mole of amine) were added to the melt. A wax emulsion was prepared, mixed and examined as described in Example 3. The intrinsic gloss amounted to 43%, the light transmittance to 80.0%. 50 55 60 65

Tests.

The following Table lists various properties of the waxes prepared in the above four Examples, as well as the temperature at which they were processed into emulsions and various properties of the resulting emulsions. 70

The light transmittance of the wax emulsions was determined in a spectrophotometer ELCO II of Messrs. Zeiss against water at a wave length of 633 nm, a layer thickness of 1.00 cm and a temperature of 20°C. The wax emulsion was diluted with distilled water at a ratio of 1:100. 75

The intrinsic gloss of the wax emulsion was determined by mixing 85 parts of the 15% wax emulsion with 15 parts of a 15% ammoniacal solution of a colophonium-maleic resin. 0.2 ml/100 cm² of this mixture was applied to a black floor tile of vinyl asbestos. The intrinsic gloss was measured by means of a gloss measuring apparatus, according to Dr. B. Lange, against a black glass plate (100% gloss). 80 85

TABLE

Example	1	2	3	4
Colour	nearly white	brown	yellowish	yellowish
Acid number	9	5	5	3
Saponification number	9	17	31	34
Density	0.966	0.978	0.974	0.980
Viscosity at 120°C in cP	2,000	2,100	110	150
Possibility of being transformed into scales	none	none	existing	existing
Emulsifying capacity	poor	poor	good	good
Processing temperature °C	120—125	120—125	115—120	115—120
Aspect of the emulsion	conglomerated	conglomerated	finely dispersed	finely dispersed
Light transmittance %	non-determinable	non-determinable	80.2	80.0
Intrinsic gloss %	non-determinable	non-determinable	48	43

Example 5.

5 A self-polishing emulsion, suitable for practical use, was prepared by mixing the following components in the indicated sequence. The plastifiers were stirred in for 30 minutes.

40.0 parts of wax emulsion prepared as in Example 3,

10 10.0 parts of an ammoniacal solution of a colophonium-maleic resin having a 15% solids content,

60.0 parts of a styrene-acrylic copolymer dispersion having a 15% solids content and a minimum film-forming temperature of about 40°C,

15 1.0 part of tributoxy-ethylphosphate, 1.5 parts of methyl diglycol, 0.5 part of pyrrolidone-2, and

20 1.0 part of an aqueous 1% solution of a fluorinated carboxylic acid, thus making 114.1 parts of self-polishing emulsion.

The intrinsic gloss of the wax film was 83%.

Example 6.

25 A self-polishing emulsion, containing a higher amount of polymer dispersion, was prepared by mixing the following components:

20.0 parts of wax emulsion prepared as in Example 3,

10.0 parts of an ammoniacal solution of a colophonium-maleic resin having a 15% solids content,

80.0 parts of a styrene-acrylic copolymer dispersion having a 15% solids content and a minimum film-forming temperature of about 40°C,

1.7 parts of tributoxy-ethylphosphate, 2.0 parts of methyl diglycol, 0.5 part of pyrrolidone-2, and

1.0 part of an aqueous 1% solution of a fluorinated carboxylic acid, thus making 115.0 parts of self-polishing emulsion.

The intrinsic gloss of the wax film was 80%.

Example 7.

45 A metal-salt containing, self-polishing emulsion, yielding detergent-proof films resistant to wear and tear, which can be easily removed by means of ammonia-containing cleaning agents, was formulated from the following components:

20.0 parts of wax emulsion prepared as in Example 3,

10.0 parts of an ammoniacal solution of a colophonium-maleic resin having a 15% solids content,

- 80.0 parts of a metal salt containing styrene-acrylic copolymer dispersion having a 15% solids content and a minimum film-forming temperature of about 40°C,
- 5 1.1 parts of tributoxo-ethylphosphate, 2.0 parts of methyl diglycol, 0.5 part of pyrrolidone-2, and 1.0 part of an aqueous 1% solution of a fluorinated carboxylic acid, thus making
- 10 114.6 parts of metal salt containing self-polishing emulsion.
- The intrinsic gloss of the wax film was 88%.
- WHAT WE CLAIM IS:—**
- 15 1. A wax comprising:
- (a) from 10 to 65% of an oxidized ethylene polymer or of a copolymer of ethylene and unsaturated fatty acid units, having a dropping point of from 95 to 115°C, an acid number of from 3 to 90, and a molecular weight of from 1500 to 4000;
- 20 (b) from 10 to 65% of an ester wax having an acid number of from 4 to 80;
- 25 (c) from 15 to 65% of a hydrocarbon wax; and
- (d) from 5 to 25% of at least one polyethylene glycol ether of (i) an alkylphenol having from 3 to 16 carbon atoms in the alkyl moiety or (ii) a fatty amine having from 8 to 24 carbon atoms, or (iii) a fatty alcohol having from 8 to 24 carbon atoms;
- 30 components (a) and (b) having been saponified with from 0.8 to 3.2% of potassium hydroxide, and all the percentages being based on the total weight of components (a), (b), and (c).
2. A wax as claimed in claim 1, wherein component (a) has an acid number of from 10 to 50.
- 40 3. A wax as claimed in claim 1 or claim 2, wherein component (a) is a copolymer of ethylene and crotonic acid, acrylic acid or methacrylic acid.
- 45 4. A wax as claimed in any one of claims 1 to 3, wherein component (b) has an acid number of from 20 to 40.
- 50 5. A wax as claimed in any one of claims 1 to 4, wherein component (b) is obtainable by esterification of an oxidation product of crude montan wax with a monohydric or polyhydric alcohol.
6. A wax as claimed in any one of claims 1 to 4, wherein component (b) is a natural wax.
- 55 7. A wax as claimed in claim 6, wherein component (b) comprises carnauba wax.
8. A wax as claimed in any one of claims 1 to 7, wherein component (c) is a hard non-oxidised hydrocarbon wax.
- 60 9. A wax as claimed in any one of claims 1 to 8, wherein component (c) is made from crude oil.
10. A wax as claimed in any one of claims 1 to 9, wherein component (c) is a micro-crystalline wax.
11. A wax as claimed in any one of claims 1 to 10, wherein component (c) has a melting point of from 80 to 90°C.
- 70 12. A wax as claimed in any one of claims 1 to 11, wherein component (c) has a density (at 20°C) of from 0.93 to 0.95 g/cm³.
13. A wax as claimed in any one of claims 1 to 12, wherein component (c) has a penetration number of from 4 to 10.
- 75 14. A wax as claimed in any one of claims 1 to 13, wherein component (d) comprises at least one polyethylene glycol ether of one of the following: nonylphenol, tributylphenol, stearylamine, oleylamine, coconut fatty amine, stearyl alcohol, tallow fatty alcohol and *iso*-tridecyl alcohol.
15. A wax as claimed in any one of claims 1 to 14, wherein component (d) contains from 4 to 30 moles of ethylene oxide per mole of phenol, amine or alcohol.
- 80 16. A wax as claimed in any one of claims 1 to 15, wherein component (d) comprises at least two polyethylene glycol ethers.
17. A process for the preparation of a wax, which process comprises mixing components (a), (b) and (c), as defined in claim 1 in the amounts there specified, saponifying the mixture with the specified amount of potassium hydroxide, and, either before or after the saponification or before and after the saponification, mixing component (d), as defined in claim 1 in the amount there specified, with the mixture.
- 90 18. A process as claimed in claim 17, wherein the potassium hydroxide is used as an aqueous solution.
19. A process as claimed in claim 17 or claim 18, wherein the saponification is effected at from 105 to 120°C.
- 105 20. A process as claimed in any one of claims 17 to 19, wherein, after saponification, the mixture is heated to about 125°C.
21. A process as claimed in any one of claims 17 to 20, wherein, after saponification, the mixture is heated at reduced pressure.
- 110 22. A process as claimed in any one of claims 17 to 21, wherein component (a) is as defined in claim 2 or claim 3.
23. A process as claimed in any one of claims 17 to 22, wherein component (b) is as defined in any one of claims 4 to 7.
- 115 24. A process as claimed in any one of claims 17 to 23, wherein component (c) is as defined in any one of claims 8 to 13.
25. A process as claimed in any one of claims 17 to 24, wherein component (d) is as defined in any one of claims 14 to 16.
- 120 26. A process as claimed in claim 17, conducted substantially as described in Example 3 or Example 4 herein.
- 125 27. A wax prepared by a process as claimed in any one of claims 17 to 26.

28. A wax as claimed in any one of claims 1 to 16, and 27, having a melt viscosity of from 40 to 700 cP (120°C).
- 5 29. A wax as claimed in claim 28, having a melt viscosity of from 70 to 500 cP (120°C).
30. An emulsion comprising a wax as claimed in any one of claims 1 to 16 and 27 to 29.
- 10 31. A self-polishing emulsion comprising a wax as claimed in any one of claims 1 to 17 and 27 to 30.
32. An emulsion as claimed in claim 31, additionally comprising at least one of the following: a polymer dispersion, a wetting and levelling agent, a plastifier, a preservative, a metal salt, an anti-corrosion agent, an anti-freeze agent, and a surface-active substance. 15

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.